Application of Biochar for Soil Remediation

Tom Sizmur,* Richard Quilliam, Aline Peregrina Puga, Eduardo Moreno-Jiménez, Luke Beesley, and Jose L. Gomez-Eyles

Abstract

Research into the use of biochar for the remediation of contaminated soils has expanded rapidly over the past 5 yr. We review recent developments in the field and present the findings emanating from small-scale batch sorption experiments, through soil incubations and bioassays, to large-scale field experiments. We discuss the evidence that these experiments have contributed toward a mechanistic understanding of how biochar is capable of remediating soils contaminated with both organic and inorganic contaminants. The effects of biochar pyrolysis temperature, biochar source material, soil type, and contaminant type on the performance of biochars for remediation are identified. The risks associated with applying biochar to uncontaminated agricultural soils are discussed. Knowledge gaps and questions are identified which, if addressed, will considerably advance the application of biochar as a soil remediation tool in the future.

Abbreviations: AC, activated carbon; DOC, dissolved organic carbon; EDTA, ethylenediaminetetraacetic acid; EVA, ethyl vinyl acetate; HOC, hydrophobic organic contaminant; PAH, polycyclic aromatic hydrocarbons; TECAM, triolein-embedded cellulose acetate membranes.

T. Sizmur, Soil Research Centre, Dep. of Geography and Environmental Science, School of Archaeology, Geography and Environmental Science, Univ. of Reading, UK; R. Quilliam, Biological & Environmental Sciences, Univ. of Stirling, Stirling, FK9 4LA, UK (richard.quilliam@stir.ac.uk); A.P. Puga, Instituto Agronômico de Campinas, Avenida Barão de Itapura, 1481, CEP 13012-970, Campinas (SP), 13020-902, Brazil (linepuga@gmail.com); E. Moreno-Jiménez, Universidad Autónoma de Madrid, 28049 Madrid, Spain (eduardo.moreno@uam.es); L. Beesley, The James Hutton Institute, Craigiebuckler, Aberdeen, AB15 8QH, UK (luke.beesley@hutton.ac.uk); and J.L. Gomez-Eyles, Integral Consulting Inc., 719 2nd Ave., Suite 700, Seattle, WA 98104 (jgeyles@integral-corp.com). *Corresponding author (t.sizmur@reading.ac.uk)..

doi:10.2136/sssaspecpub63.2014.0075

Agricultural and Environmental Applications of Biochar: Advances and Barriers. SSSA Special Publication 63. M. Guo, Z. He, and M. Uchimiya, editors.

Biochars possess a number of remarkable properties that make them suitable for the remediation of contaminated soils, including a high internal surface area, negative charge, and resistance to degradation. Generally, the higher the temperature that organic material is pyrolyzed, the higher the surface area of the resulting biochar (Gomez-Eyles et al., 2013a), although there is evidence that some biochar pores collapse and decrease surface area at very high pyrolysis temperatures (Lua and Guo, 1998). There is a considerable negative charge over the surface of biochar (Mukherjee et al., 2011), which attracts positively charged metals and organic compounds to the internal biochar surface from the soil solution. In doing so, the concentration of metals and organic contaminants in the soil solution can be reduced (Beesley et al., 2010), along with their current availability for uptake by organisms (i.e., their bioavailability [Semple et al., 2004]), or their potential to become available for uptake by organisms (i.e., their bioaccessibility [Semple et al., 2004; Gomez-Eyles et al., 2011; Houben et al., 2013a]).

The surface of biochars produced during pyrolysis at lower temperatures (200–400°C) are rich in "oxygen-containing functional groups" that enable the creation of surface complexes between cations (e.g., Cu^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, and Zn^{2+}) and the biochar surface (Beesley and Marmiroli, 2011; Uchimiya et al., 2011a). This negative charge can also increase soil pH after biochar application to contaminated soils because the negative surface attracts hydrogen ions from the soil solution. A higher soil pH serves to further increase the sorption of metals from solution because of the deprotonation of pH-dependent cation exchange sites on soil surfaces (Rees et al., 2014b), especially in acidic soils.

Some biochars contain a considerable mineral ash component (e.g., up to 50% for manure manure-derived, or even 85% for bone meal–derived source materials [Amonette and Joseph, 2009]). Minerals such as carbonates, phosphates, and sulfates can cause some toxic elements (e.g., Pb) to precipitate out of solution. Because the precipitates are rather insoluble (especially Pb salts, and especially at high pH), this mechanism can contribute considerably to the remediative capacity of biochars (Cao et al., 2009).

Finally, biochar degrades very slowly with predicted C half-lives ranging from 10^2 to 10^7 yr (Zimmerman, 2010). Therefore, during the timescales that most soil remediation projects operate (~10 to 100 yr), biochar can be considered an inert material. An advantage of this recalcitrance is the potential to sequester soil contaminants for a long period of time. However, oxygen-containing functional groups on the surface of the biochar may release cations into solution over time as they are replaced with hydrogen ions (Kim et al., 2013).

Why Biochar Is a Suitable Soil Amendment for Remediation of Contaminated Soil

The objective of contaminated land remediation projects is to reduce the risk of harm that contaminants could cause to organisms. This is achieved by breaking or reducing source-pathway-receptor linkages (Bardos et al., 2002) (Fig. 1). A source is the physical location of a contaminant itself, or the location from which it is being emitted. A receptor is the location where it can cause harm (e.g., human tissue, other organisms, or water bodies). The pathway is the mechanism by which the contaminant moves from the source to the receptor. When a contaminant can move from a source to a receptor in sufficient doses to cause harm, then the contaminant

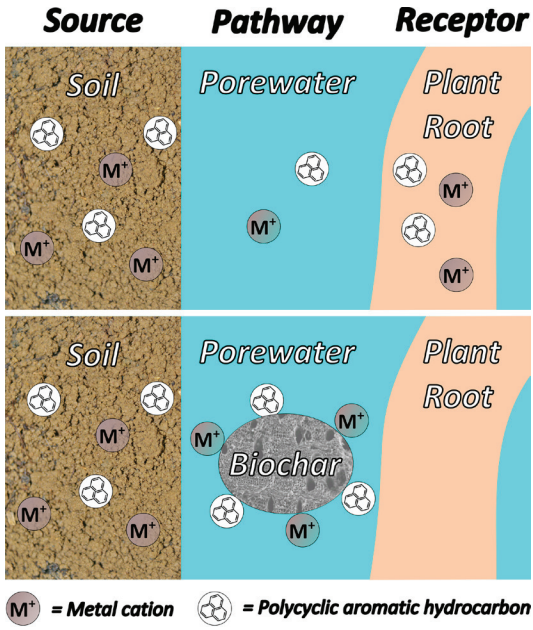

Fig. 1. Diagram to demonstrate the remediation of organic and inorganic contaminants in soil by biochar, breaking a source-pathway-receptor linkage.

is considered a pollutant and the soil is considered polluted soil. In many cases the simplest (and most cost effective) method to remediate polluted soil is to remove the source of a contaminant (e.g., excavate it and deposit it elsewhere), or to remove the receptor (e.g., put a fence around the site to restrict access). However, these propositions are often impractical and expensive when widespread soil contamination occurs or when a contaminated site is in active use.

There are many pathways by which contaminants in soils may migrate from sources to receptors but most require the dissolution of a contaminant into the soil solution. Biochar breaks source-pathway-linkages by adsorbing contaminants on its surface and thereby reducing the concentration of contaminants in the soil solution (Beesley and Marmiroli, 2011). Remediation is achieved if biochar irreversibly adsorbs contaminants that come into the soil solution, eliminating the pathway to receptors (Fig. 1). After sorption on the surface of the biochar, contaminants can be considered unavailable to organisms and no longer pose a risk of causing harm.

Comparison of Biochar and Activated Carbon

Like biochar, activated carbon (AC) is produced by pyrolysis, usually of coal, but also waste biomass products like coconut shells. However, an extra activation step is involved in its manufacture usually using steam (Rittenhouse et al., 2014) but also chemicals (e.g., phosphoric acid (Lim et al., 2010), chitosan (Zhou et al., 2013), potassium hydroxide (Regmi et al., 2012), or hydrogen peroxide (Xue et al., 2012)). This activation further develops the inner pore structure of the carbons giving it a superior surface area (generally >900 m^2/g N_2 BET) relative to biochar (generally 1–350 m^2/g N_2 BET). This makes AC more favorable for the remediation of

hydrophobic organic contaminants (HOCs) because HOCs generally have greater affinity for higher surface area carbons (Cao et al., 2011; Gomez-Eyles et al., 2013a; Rittenhouse et al., 2014). The use of AC to break pollutant pathways has provided a new direction in the remediation of contaminated sediments, especially those impacted with HOCs (Ghosh et al., 2011), and is currently being deployed by the sediment remediation industry after successful reductions of HOC bioavailability in field pilots (Beckingham and Ghosh, 2011; Cho et al., 2012).

Given the superior surface area and sorption capacity of ACs relative to biochars, ACs have been recommended as the most appropriate carbon amendment for the remediation of HOC-impacted sediments (Gomez-Eyles et al., 2013b). However, when produced in bulk, biochar is cheaper than AC (<USD$1000 per ton vs. USD$2500 per ton) and is often produced from waste resources. Furthermore, biochar can be less detrimental to soil biota health than AC (Hale et al., 2013), and can be more effective at stimulating plant growth than AC because of enhancements in soil quality (Denyes et al., 2013). Biochar is also generally less dense than AC, which could favor the kinetics of contaminant mass transfer from the soil to the carbon as there are a higher number of particles per unit mass relative to AC if they are amended at the same dose and particle size. However, ACs will still possess a higher number of sorption sites for HOCs per unit mass and are therefore likely to be more effective at reducing HOC bioavailability in most soils. Most comparative studies between the two have shown superior performance of the AC for HOCs (Cao et al., 2009; Cao et al., 2011; Gomez-Eyles et al., 2013b; Hale et al., 2012; Rittenhouse et al., 2014). However, in a recent field pilot their performance was not statistically different (Denyes et al., 2013). On the other hand, most comparative studies between the two for inorganic contaminants showed superior performance by the biochar relative to the AC (Cao et al., 2009, 2011), although this was not the case for mercury (Gomez-Eyles et al., 2013b). Optimum amendment choice will therefore depend of the contaminants of concern and may vary between different soils. Treatability studies using site-specific soils could be performed to aid amendment selection.

The Research Scientist's Toolbox

As research scientists developing techniques for the remediation of contaminated soils with biochar, we have a number of tools and techniques available to us. Research on the remediation of contaminated soils with biochar can take place at a variety of scales. These range from highly controlled microcosm environments in the laboratory to field experiments conducted under prevailing ambient conditions. Environmental research usually evolves from the laboratory to the field, often alongside a reduction in the number of treatments tested. In this chapter we will highlight recent literature and discuss the contribution that each of the following experimental approaches (summarized in Table 1) have made to our understanding of the science behind the application of biochar for soil remediation.

- Batch sorption studies
- Biochar–soil incubations
- Bioassays
- Field experiments

Table 1. A critical summary of the experimental approaches employed by soil scientists to investigate the application of biochar for soil remediation.

Experimental approach	Description	Information approach can provide	Limitations of approach
Batch sorption studies	Biochar is mixed with an artificial contaminated solution under standard conditions. Quantity of contaminants removed from solution by biochar is quantified.	Useful as a method to screen biochars with superior sorption capacity and investigate the mechanisms by which sorption of contaminants by biochar occurs.	Does not adequately represent the conditions to which biochar is exposed under field conditions. Overestimation of sorption capacity may result from greater contact between biochar and contaminants than is possible in the field.
Biochar–soil incubations	Biochar is mixed with contaminated soils, and then the biochar-soil mixture is chemically extracted or incubated with passive samplers to quantify the mobility and/or bioavailability of the contaminants in the "remediated" soil.	Information on both desorption from soils and sorption on biochar is obtained. Useful to screen different biochars to remediate a particular soil and for investigating biochar, soil, and contaminant interactions (e.g., interactions due to changes in pH electrical conductivity and redox potential).	Some chemical extractions may not always provide a good indication of bioavailability for certain contaminants difficult to separate direct from indirect effects of biochar on contaminant mobility. If the soil–biochar mixture is mixed mechanically for prolonged periods (e.g., to achieve passive sampler equilibration), contaminant mass transfer will be enhanced. This could lead to an overestimation of the short-term efficacy of the biochar in the field.
Bioassays	Biochar is mixed with contaminated soil and exposed to an organism (e.g., plant or earthworm), and either the uptake of contaminants, growth rate, or symptoms of toxicity to the organism are assessed.	Allows assessment of the effect of biochar to ecologically relevant organisms. Allows the effect of the organism on the fate of the contaminant in the biochar–soil mixture to be assessed.	Subject to the variability associated with the culture of test organisms. Direct effects of the biochar on the organism (e.g., improving soil fertility) can mask effects that are due to alteration of contaminant availability.
Field experiments	Biochar is applied to the surface or incorporated into designated plots of land at specified rates and then measurements can be made on soil and plant properties in the individual plots.	Applications are exposed to prevailing ambient conditions and provide the best opportunity to simulate the real remediation performance of a biochar.	Expensive and time consuming to perform so can only be applied to a limited number of treatments. Temporal and spatial variability makes mechanistic interpretations of observations difficult. Choosing the application method and form of biochar is difficult (e.g., particle shape, pellets, size, and moisture).

Batch Sorption Studies

Batch sorption experiments enable researchers to quantify the capacity of a biochar to adsorb contaminants from a solution. Biochar is mixed with a solution containing a known concentration of a contaminant for a known time period under controlled temperature conditions. For metals and readily soluble organic contaminants the solution can be separated from the biochar (usually by centrifugation and/or filtration). The concentration of contaminant remaining in solution is then measured. For HOCs, detection can be more challenging because of the extremely low concentrations of these chemicals in the freely dissolved phase. Instead, equilibrium passive sampling methods are employed. Plastic polymers submerged in the solution accumulate HOCs and can be used to infer freely dissolved concentrations (Ghosh et al., 2014). The difference between the concentration at the start and the end of the incubation is used to infer the quantity of contaminant adsorbed to the surface of the biochar. The concentration of pollutants that are adsorbed is calculated by subtracting the end concentration from the concentration at the start.

Sorption Isotherms

By determining the quantity of contaminant adsorbed to the biochar surface at constant temperature and a range of contaminant concentrations, an adsorption isotherm can be generated. The adsorption isotherm can then be fitted to a model. The two most common models for fitting sorption isotherms on biochars are the Freundlich and Langmuir models (Fig. 2). The Langmuir model assumes that the adsorbate forms a monolayer over a homogenous surface (Sparks, 2003). The model assumes that there is a maximum number of identical sites where sorption can occur. Therefore, the maximum adsorption capacity of a given biochar can be derived by fitting the model to experimental data. Comparing the adsorption capacities of different biochars allows researchers to predict their relative performance at reducing the bioavailability of contaminants in soils. For example, Chen et al. (2011) showed that the maximum Cu and Zn sorption capacities of a 450°C pyrolyzed corn straw–derived biochar was double that of a hardwood-derived biochar pyrolyzed at 600°C. Gomez-Eyles et al. (2013b) also conducted a series of sorption isotherms to evaluate biochar sorption capacity of HOCs, mercury, and methylmercury relative to ACs. The Langmuir model has recently been fitted to batch sorption data for several biochar source materials, but mostly inorganic contaminants and often in combination with the Freundlich model (Table 2).

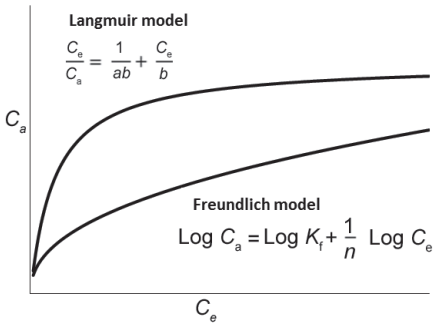

Fig. 2. Idealized Langmuir and Freundlich models for the adsorption of contaminants on the surface of biochar. C_a is the concentration of contaminant adsorbed on the biochar, C_e is the equilibrium concentration of contaminant in solution, b is the Langmuir maximum adsorption capacity, K_f represents the Freundlich relative sorption capacity, n and a are adsorption constants for the Freundlich and Langmuir models, respectively.

Table 2. A summary of recent publications that fit batch sorption data to Langmuir and/or Freundlich models.†

Biochar source material	Contaminant(s)	Model(s) fitted	R^2	Reference
Meat and bone meal	Zn	Langmuir	0.825	Betts et al. (2013)
Swine manure	Cr(III)	Langmuir and Freundlich	0.641–0.999 0.636–0.996	Wnetrzak et al. (2014)
Almond shell	Ni and Co	Langmuir and Freundlich	0.989–1.000 0.896–0.995	Kılıç et al. (2013)
Rice husk and dairy manure	Pb, Cu, Zn, and Cd	Langmuir and Freundlich	Rice husk: 0.96–0.99 Dairy manure: 0.74–0.98 Rice husk: 0.82–0.89 Dairy manure: 0.86–0.97	Xu et al. (2013)
Swine and dairy manure	Cu, Zn, Cd and Pb	Langmuir and Freundlich	Swine manure: 0.979–0.999 Dairy manure: 0.969–0.999 Swine manure: 0.821- 0.997 Dairy manure: 0.765–0.994	Kołodyńska et al. (2012)
Sawdust	Methyl blue	Langmuir and Freundlich	0.994 0.865	Wang et al. (2013)
Municipal waste	As(V)	Langmuir and Freundlich	0.961–0.992 0. 859–0.995	Jin et al. (2014)
Crop residues	Cd	Freundlich	0.939–0.964	Sun et al. (2014)
Tree bark and vine shoot	Cd, Cu, Ni, Pb, and Zn	Freundlich	Tree bark: 0.94–0.99 Vine shoot: 0.98–0.99	Venegas et al. (2015)
Wheat straw	Hexachlorobenzene	Freundlich	0.93	Song et al. (2012)
Cottonseed Hull	Deisopropylatrazine	Freundlich	0.99–0.84	Uchimiya et al. (2012)
Beech wood	Imazamox, methyl-desphenyl-chloridazon, metazachlor oxalic acid, and metazachlor sulfonic acid	Freundlich	>0.95	Dechene et al. (2014)
Maple wood	Napthalene, Benzene and 1,4-dinitrobenzene	Freundlich	0.85–0.99	Lattao et al. (2014)
Pine wood, peanut hull, hardwood, acai pit, poultry litter, and phragmites	PCBs, PAHs, and DDTs	Freundlich	0.50–1.0	Gomez-Eyles et al. (2013)

† R^2 values are given for each model in line with the Model(s) fitted column. Level of precision reflects that reported in the referenced publication.

The Freundlich model is an empirical equation that has the advantage of allowing different sorption sites to have different adsorption energies (Sparks, 2003). The sites with the highest adsorption energy "fill up" first. This allows the model to be applied to adsorption on heterogeneous surfaces. The Freundlich model has been recently used to model the sorption of a large range of organic and inorganic contaminants to biochars produced from several different source materials (Table 2). However, the Freundlich equation does not allow the calculation of a maximum adsorption capacity. Several recent papers publish the constants associated with both the Langmuir and Freundlich models fitted to experimental data on the sorption of contaminants to biochar (Table 2).

Batch Sorption Studies to Elucidate Biochar Sorption Mechanisms

Batch sorption studies can also be very useful to improve our mechanistic understanding of how contaminants sorb to biochar. Better understanding these mechanisms is important as biochar production parameters (e.g., source material, final pyrolysis temperature, heating rate, and duration or surrounding gases) can be manipulated to produce biochars with optimum characteristics (e.g., surface area, pore size distribution, and surface chemistry) for the sorption of a contaminant of concern (Lattao et al., 2014; Sun et al., 2012a; Uchimiya et al., 2011b).

The maximum metal sorption capacity of a biochar generally increases with pyrolysis temperature to a peak around 350–400°C, after which sorption decreases with pyrolysis temperature (Kołodyńska et al., 2012; Uchimiya et al., 2011b; Zhang et al., 2013a). This peak is concurrent with a peak in the cation exchange capacity of biochar found in the same temperature range (Gomez-Eyles et al., 2013a). Several studies report contrasting mechanisms of metal sorption between high and low pyrolysis temperature biochars (Dong et al., 2013; Gomez-Eyles et al., 2013a; Harvey et al., 2011; Uchimiya et al., 2010). Metal sorption on low-temperature biochars primarily occurs because of ion exchange with oxygen-containing functional groups such as hydroxyls, carboxyls, and phenols (Dong et al., 2013). After high-temperature pyrolysis, the C/O ratio of the biochar increases (Uchimiya et al., 2011b) and the surface becomes more electronegative (Fig. 3). Consequently, metal sorption primarily occurs because of an electrostatic interaction between the positively charged metal ions and negative charge associated with delocalised π-electrons on aromatic structures (Harvey et al., 2011). The chemisorption of metals by inner sphere complex formation is generally much stronger than the physisorption of metals via cation–π interactions.

In general, biochars with higher surface areas have an enhanced ability to sorb HOCs, and increasing pyrolysis temperatures can enhance biochar surface area (Gomez-Eyles et al., 2013a) (Fig. 3), although there is some evidence that biochar pores collapse and decrease surface area at very high pyrolysis temperatures (Lua and Guo, 1998). For example, by keeping all other production parameters constant, Chen et al. (2008) clearly demonstrate how increasing pyrolysis temperature increased BET-N_2 surface area, and this in turn favored the sorption of naphthalene and nitrobenzenes. However, BET-N_2 surface area on its own cannot fully predict HOC sorption to carbons (Bucheli and Gustafsson, 2000; Chun et al., 2004; Wang and Xing, 2007). Pignatello et al. (2006) point out how N_2 sorption isotherms performed at 77 K can provide a good measure of biochar mesoporosity, but fail to quantify microporosity as N_2 diffusion into micropores is severely limited at these temperatures. Instead, the authors couple the use of

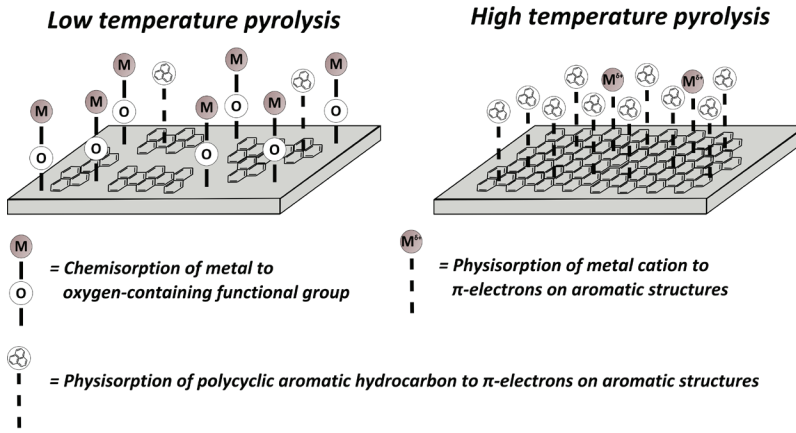

Fig. 3. Conceptual diagram depicting the mechanisms of organic and inorganic contaminant sorption to high-temperature and low-temperature biochar. After low-temperature pyrolysis (300–500°C) a high density of oxygenated functional groups provides cation exchange sites for optimal metal sorption. After high-temperature pyrolysis (>500°C) the biochar increases in aromaticity and there is greater sorption of organic compounds by cation–π interactions.

77 K N_2 isotherms with CO_2 sorption isotherms conducted at 273 K to get an accurate measurement of both meso- and microporosity. Lattao et al. (2014) used measures of both of these parameters and others likely to affect HOC sorption to biochar in a comprehensive study to better understand the factors controlling sorption. All these parameters on their own failed to predict sorption, although a model relating sorption to a weighted sum of micro- and mesoporosity was more successful. Hydrophobic organic contaminant sorption therefore depends on a complex interrelationship between the contaminant properties (e.g., hydrophobicity, polarity, and steric size and/or shape) and the biochar properties. Further studies are needed to better understand these relationships so biochar production from remediation purposes can be optimized.

Summary

Batch sorption experiments and the fitting of adsorption isotherm models (e.g., the Langmuir and Freundlich models) have enabled researchers to observe the effects of biochar production parameters (e.g., pyrolysis temperature and source material) on the sorption capacity of the resulting biochar. Furthermore, combination with complimentary biochar characterization (e.g., C/O ratio and surface area) has improved our understanding of the mechanisms of sorption.

Biochar–Soil Incubations

Laboratory incubations of biochar–soil mixtures enable us to test the performance of a biochar as a soil amendment to reduce contaminant mobility. Incubations offer advantages over batch sorption studies because they capture both the (i) desorption of contaminants from the soil surface and (ii) adsorption of contaminants on the surface of the biochar. Batch sorption experiments only assess the latter.

Therefore, soil–biochar incubations are likely to provide more robust predictions of biochar remediation performance in the field, if they are performed using field contaminated soils. Like batch sorption studies, conditions (e.g., temperature and moisture) are often well controlled to ensure reproducibility. Typically, biochar is mixed with a contaminated soil and incubated at a given moisture content for a known period of time. The mobility of the contaminant in the soil–biochar mix is then determined by extracting a known quantity of the soil with an aqueous solution or mild solvent (e.g., $CaCl_2$, chelating agents, butanol, methanol, or acids) or an infinite hydrophobic sink (e.g., cyclodextrin or Tenax) to predict the contaminant fraction that can become available for uptake or degradation (Reichenberg and Mayer, 2006). The concentration of contaminant present in the extraction solution can then be determined analytically. There is consensus in more recent work that measuring freely dissolved concentrations of organic and inorganic contaminants with passive samplers (e.g., solid-phase micro extraction [Jonker et al., 2007], polyethylene [Adams et al., 2007], POM [polyoxymethylene] [Jonker and Koelmans, 2001], ethyl vinyl acetate [EVA] [Andrade et al., 2014], triolein-embedded cellulose acetate membranes [TECAM] [Tao et al., 2009], or diffusive gradients in thin films [Zhang et al., 2001]) can provide the best indication of the actual bioavailability of contaminants in soils (Gomez-Eyles et al., 2012; Nolan et al., 2005). These methods enable an assessment of the efficacy of a particular biochar by its ability to reduce the mobility or availability of contaminants in contaminated soils.

Chemical Methods to Assess Contaminant Mobility and Availability in Soil–Biochar Mixtures

Column-leaching experiments have been widely adopted to determine the effect of biochar on the mobility of contaminants in soils. Experiments can involve the one-time introduction of water to the top of a column containing a soil–biochar mix or the circulation of water through a column until equilibrium is reached. Beesley and Marmiroli (2011) constructed flow-through columns to determine the capability of biochar to immobilize Cd and Zn. Although considerable dissolved carbon was leached from the soil–biochar mix, Cd and Zn were immobilized and the immobilization could not be reversed by leaching with water at pH 5.5. The leachability of pentachlorophenol from soil was assessed in a column-leaching experiment and was reduced by 43% after amendment with bamboo biochar (Xu et al., 2012). Cabrera et al. (2011) showed that biochars with higher surface areas decreased the leaching of the herbicides fluometuron and 4-chloro-2-methylphenoxyacetic acid in an agricultural soil.

Soil porewater can be extracted from soils with Rhizon soil moisture samplers which mimic the uptake of water by plant roots. The concentration of contaminants in the extracted porewater can be determined analytically. Rhizon samplers enable repeated extraction of porewater from pots, columns, or soil pits with minimal disturbance of the soil profile. They consist of a porous plastic material connected to a tube to which a vacuum can be applied to draw water out of the soil. The samplers can be inserted horizontally into pots or columns through predrilled holes and remain in place for the duration of an experiment, enabling repeat sampling (Karami et al., 2011; Sizmur et al., 2011c). Beesley et al. (2010) showed that biochar consistently reduced Cd concentrations 10-fold in porewater samples extracted from a multi-element polluted soil with Rhizon samplers.

Park et al. (2011) used Rhizon samplers to repeatedly collect porewater from pots amended with chicken manure and green waste–derived biochars. The biochars reduced Cd and Pb porewater concentrations but increased Cu concentrations. In contrast, Karami et al. (2011) showed that biochar reduced porewater Cu concentrations when sampled every 4 wk with Rhizon samplers inserted in pots.

Equilibrium passive samplers can be used to infer the freely dissolved concentration of HOCs in the soil porewater which ultimately determines its equilibrium partitioning concentration in soil organisms (Gomez-Eyles et al., 2012; Reichenberg and Mayer, 2006). Polyoxymethylene and EVA have been used to evaluate biochar effectiveness at reducing polycyclic aromatic hydrocarbons (PAHs) and organochlorine bioavailability. No significant reduction in PAH concentrations in porewater were found by Brennan et al. (2014b), and only slight reductions in some DDT (dichlorodiphenyltrichloroethane) metabolites were reported by Andrade et al. (2014). However, Wang et al. (2013) measured reduced bioavailability of PCBs (polychlorinated biphenyls) using TECAM, and these reductions correlated strongly with reductions in uptake by plant roots.

Chemical extractions are often used to determine the bioavailability of contaminants in soils or soil–biochar mixtures (Gomez-Eyles et al., 2010; Rittenhouse et al., 2014; Xu et al., 2012). These extractions have the disadvantage that the amount of contaminant extracted is dependent on the strength of the solvent selected, and not only on the bioavailability of the contaminant. Extractions involve agitating a sample in a known volume of extractant solution for a known period of time, then centrifuging and/or filtering to separate the solid and solution phases. The concentration of metals in the solution is then determined analytically. Farrell et al. (2013) compared five different chemical extractions (water, 0.01 M $CaCl_2$, 0.05M ethylenediaminetetraacetic acid [EDTA], 0.5 M acetic acid, and 1 M NH_4NO_3) to determine which was the most suitable for predicting plant uptake. None of the extractions were deemed suitable for multi-element polluted soils but EDTA, acetic acid, and water extractions were each significantly correlated with three metals (EDTA and acetic acid were correlated with Mo, As, and Cd, while water was correlated with Mo, As, and Pb). Water extractions were also used by Gomez-Eyles et al. (2011) to reveal a reduction in Cu mobility due to biochar amendment concurrently with a reduction in Cu uptake by earthworms. Large reductions in water extractable Cu, Pb, and Zn were also found after biochar addition to a mine soil (Sizmur et al., 2011e). Xu et al. (2012) reported 56 and 65% reduction in distilled water and methanol extractable pentachlorophenol after biochar amendment. A popular choice of extracting solution is 0.01 M $CaCl_2$ because it has a similar ionic strength as soil porewater (Houba et al., 2000). Calcium chloride has been used to show that biochar reduces extractable Co, Cu, and Ni in a depleted mine soil (Rodríguez-Vila et al., 2014), reduces Cd, Zn, and Pb bioavailability in a smelter-impacted soil (Houben et al., 2013b), and reduces Cd availability in contaminated rice paddies (Cui et al., 2011) and wheat fields (Cui et al., 2012). Cao et al. (2011) found amending a soil with a dairy-manure-derived biochar reduced 0.01 M $CaCl_2$ extractable atrazine by 66 to 81%. EDTA is a chelating agent capable of binding considerable concentrations of metals in solution. An EDTA extraction was used to demonstrate that a sewage sludge biochar reduced the bioavailability of As, Cr, Co, Ni, and Pb (but not Cd, Cu, and Zn) in a contaminated rice paddy soil (Khan et al., 2013). Ethylenediaminetetraacetic acid extractable soil Cd was

also reduced after addition of oil mallee biochar and wheat chaff biochar in Cd-contaminated soil (Zhang et al., 2013b).

Depletive sampling techniques provide an infinite hydrophobic sink that remove all organic contaminants that readily enter the soil solution, and can therefore give a measure of the "rapidly desorbing fraction." This contaminant fraction is regarded as bioaccessible (currently bioavailable + potentially bioavailable [Semple et al., 2004]), and has been shown to provide a good measure of the total amount of HOCs readily available for degradation (Cornelissen et al., 1998; Reid et al., 2000). Reductions in PAH and hexachlorobenzene bioaccessibility after biochar amendment have been measured using cyclodextrin extractions and correlate well with reductions in uptake by earthworms (Gomez-Eyles et al., 2011; Song et al., 2012). Wang et al. (2013) also reported correlations in reduced PCB bioaccessibility measured using cyclodextrin and reduced PCB bioaccumulation in plant root tissues.

Biochar–Soil–Contaminant Interactions

Biochar–soil incubations allow researchers to account for any interactions between the soil components (e.g., organic matter and minerals), the biochar, and the contaminant which are not captured in clean isotherm studies. These interactions include the fouling, for example, pore blocking and/or scavenging, of the biochar surface by organic matter that reduces their efficacy to sorb HOCs (Pignatello et al., 2006), and subsequent reductions in dissolved organic matter concentrations that are known to play a major role on the complexation of heavy metals in solution (Gomez-Eyles et al., 2011; Weng et al., 2002).

Biochar increases the pH of a contaminated soil if the pH of the biochar is greater than the pH of the soil it is added to (Beesley et al., 2010; Sizmur et al., 2011e). This is due to the creation of metal oxides from base cations (e.g., K, Ca, Si, and Mg) during pyrolysis (Novak et al., 2009). Therefore, biochar source materials with the greatest mineral concentrations result in the highest biochar ash components and have the highest pH (Lehmann et al., 2011). It is therefore intuitive that they will produce the greatest increase in soil pH following application. By increasing the soil pH, the solubility of metal cations in the soil solution decreases. As a result, metals can precipitate out of solution, particularly as phosphates (Uchimiya et al., 2010). Biochars produced from manure source materials have particularly high mineral ash contents and can immobilize considerable concentrations of metals by this mechanism (Cao and Harris, 2010, Uchimiya et al., 2010). However, high phosphate concentrations in biochar may also result in mobilization of arsenate (Beesley et al., 2014).

For a biochar to be effective in reducing contaminant bioavailability in an amended soil, it has to improve its sorptive properties. Elevating the soil pH can increase the number of pH-dependent cation exchange sites on the soil surface. Therefore, biochar removes metals from the soil solution not only by adsorbing metals on its own surface, but also by increasing the metals adsorbed by the soil itself. Houben et al. (2013b) demonstrated that the immobilization of Cd, Zn, and Pb was almost entirely due to an increase in soil pH. The metal availability (assessed with a 0.01M $CaCl_2$ extraction) was similar in control and biochar-amended soils at a given pH, but the biochar increased the acid-neutralizing capacity of the soil, effectively buffering the soil against future decreases in pH

and preventing the leaching of metals. Separating the immobilization of metals due to sorption on the biochar surface from the (pH mediated) effect of sorption on the soil surface is difficult but has been attempted by Rees et al. (2014a) who constructed a two-column experiment. Leachate was circulated sequentially through columns containing contaminated soil and biochar separately to determine the relative sorption of Cu, Pb, and Zn on both the biochar and the soil.

Biochars are likely to be more effective in soils where contaminants are more bioavailable. Superior AC effectiveness in reducing mercury and methylmercury bioavailability has been reported in sediments with lower native sediment–water partition coefficients than in sediments where the contaminants were already tightly bound (Gilmour et al., 2013). Gomez-Eyles et al. (2013b) reported much higher bioavailability reductions in PCB-impacted sediments after amendment with AC than biochar. These higher reductions in bioavailability were related to the higher sorption capacity of the ACs that were generally 1 to 2 orders of magnitude higher than the biochars. As the sorptive capacity of the sediments used in that study was already high before amendment, it was concluded that the biochars did not provide a sufficient enhancement of the sorptive properties of the native sediment, whereas the AC did. However, in other sediments or soils where the native bioavailability is lower to start off with (e.g., soils with low native organic carbon and black carbon contents) the addition of biochar amendments will have a larger impact on the sorptive capacity of the soil with a subsequent reduction in HOC bioavailability. Similarly for heavy metals, biochars have been shown to be highly effective in reducing metal mobility in sandy–acidic mine soils (Sizmur et al., 2011e), but smaller bioavailability reductions have been observed in calcerous soils where the metals are already strongly bound (Gomez-Eyles et al., 2011).

Summary

The methods used to assess the mobility of contaminants in soils are becoming increasingly sophisticated, and there is a general move toward assessing the mobility of contaminants in biochar-remediated soil with passive samplers instead of chemical extractions. Biochar applied to soil has been shown to reduce contaminant mobility in leachate, porewaters, water extractions, 0.01 M $CaCl_2$ extractions, EDTA extractions, and cyclodextrin extractions. Mixing biochar with soil also enables researchers to understand the interactions between biochars and soil and elucidate indirect mechanisms for biochar-reducing contaminant mobility. For example, the application of biochar to soil often increases the pH, which increases the pH-dependent cation exchange capacity of soils and results in higher metal removal from the soil solution.

Bioassays

Bioassays (or biological assays) employ organisms in determining the availability, uptake, and toxicity of contaminants in soils. Experiments to assess the effect of biochar on soil contaminant remediation often involve introducing organisms into contaminated soil mixed with biochar (alongside a biochar-free control soil). The growth of the organism, the uptake of contaminants by the organism, or the symptoms of toxicity expressed by the organism are then assessed. Bioassays add another layer of complexity to the systems studied in both batch sorption experiments and soil–biochar incubations. The processes that can be captured by

bioassays include (i) the desorption of contaminants from the soil surface, (ii) the adsorption of contaminants on the surface of the biochar, (iii) the uptake of contaminants by an organism, and (iv) the transport of contaminants to a site of toxic action. Bioassays are therefore better able to predict the effect of biochar on the bioavailability and toxicity of contaminants in soils than soil–biochar incubations.

The majority of bioassays conducted to demonstrate a reduction in contaminant bioavailability after biochar application use either plants or earthworms as test organisms. Both plants and earthworms are at the base of the terrestrial food chain. Therefore, reducing the uptake of contaminants to plants and earthworms minimizes trophic transfer to humans and predatory mammals and birds (Armitage and Gobas, 2007; Peralta-Videa et al., 2009). This is particularly the case for contaminants that biomagnify through food webs (e.g., methylmercury and PCBs).

Earthworms

Earthworms are important soil organisms because they regulate soil structure, accelerate the rate of organic matter decomposition, and increase nutrient availability to plants. Earthworms are therefore considered keystone species and ecosystem engineers (Jones et al., 1994; Jouquet et al., 2006). It is for these reasons that it is important to reduce the bioavailability of contaminants to earthworms to below a level where these ecosystem services are not significantly affected. Furthermore, because earthworms are easy to culture in laboratories, have intimate contact with the soil, and do not require special permits for their use in ecotoxicology, they are excellent test species for bioassays.

Significant reductions in earthworm bioaccumulation have been reported after biochar amendment for a number of contaminants including PAHs and Cu (Gomez-Eyles et al., 2011), PCBs (Denyes et al., 2012), Pb (Cao et al., 2011), atrazine (Cao et al., 2011; Wang et al., 2014), and hexachlorobenzene (Song et al., 2012). However, other studies have found no effect or very modest reductions in bioaccumulation. For example, Andrade et al. (2014) found biochar amendments had no effect or slightly increased dieldrin and 4,4′-DDT bioaccumulation in *E. fetida*. The same study reported drops in 4,4′-DDD (dichlorodiphenyldichloroethane) and 4,4′-DDE (dichlorodiphenyldichloroethylene) bioaccumulation, but these reductions were generally lower than those achieved by compost amendments. Similarly, Denyes et al. (2013) found significant reductions in PCB bioaccumulation after manually mixing AC into the soil, but not for biochars. However, significant reductions were observed for both amendments when mechanically mixing the carbons into the soils for 24 h. Gomez-Eyles et al. (2011) reported significant reductions in Cu mobility after biochar application, but not for As, Cd, Co, Ni, and Zn. These contrasting results suggest the success of biochar amendments is likely to be biochar and soil specific. Both the sorptive quality and quantity of the biochar, and the native bioavailability of the contaminants in the receiving soil, will ultimately control whether the amendment is effective. Other factors like the soil properties (e.g., organic matter content), the mixing regime, and even the earthworm species will also influence how effective biochar is in reducing earthworm bioaccumulation. Wang et al. (2014) reported larger reductions in atrazine bioaccumulation for endogeic earthworms (*Metaphire guillelmi*) that live and feed in soil than for epigeic earthworms (*Eisenia fetida*) that live and feed

in the soil litter. It was hypothesized that biochar was particularly effective at reducing atrazine absorption through the earthworm gut.

Despite reducing bioaccumulation, minor toxic effects of biochar on earthworm health have been reported. Gomez-Eyles et al. (2011) recorded a reduction in earthworm weight in a hardwood-derived biochar-amended soil contaminated with PAHs and metals relative to an unamended soil. Decreased earthworm growth rate was also observed by Jakob et al. (2012) after addition of ACs to a PAH-contaminated soil. Earthworms feed by allowing dissolved organic molecules to diffuse across their gut wall. Therefore, biochar may also reduce nutrient absorption in the earthworm gut. The more effective the biochar is at adsorbing organic molecules, the greater impact this is likely to have on earthworm growth rates.

Earthworms are known to ingest biochar (Lehmann et al., 2011) and act as mixing and dispersing agents for biochar in soils (Ameloot et al., 2013), and may therefore benefit remediation. Concurrently, the inoculation of earthworms into contaminated soils has the potential to become a commonly used practice during land remediation and restoration (Butt, 1999; Sizmur et al., 2011a). However, in the absence of biochar, earthworms can increase contaminant mobility in soils through their feeding, burrowing, and casting activities (Sizmur et al., 2011b; Sizmur et al., 2011d). Therefore, it is prudent to investigate whether earthworm activity in biochar-amended soils increases or decreases the mobility of metals. Sizmur et al. (2011e) inoculated *L. terrestris* earthworms into a former mine soil contaminated with Cu, Pb, and Zn after biochar amendment and found that the earthworms had no significant effect on the metal mobility. However, biochar application reduced the concentrations of water soluble metals by >95%, so any earthworm mediated increase in mobility may have been buffered by this very effective biochar.

Plants

Reductions in both organic and inorganic contaminant bioaccumulation have been reported in different plant species (e.g., *Cucurbita pepo*, *Brassica napus* and *Zea mays*) after biochar amendment (Brennan et al., 2014b; Denyes et al., 2012; Denyes et al., 2013; Houben et al., 2013a). However, the success of the biochar treatment is likely to depend on the factors previously discussed for earthworms (biochar sorpitive capacity, bioavailability of contaminants in soil before application, species selection, and biochar mixing regime). For example Denyes et al. (2013) found that the biochar amendment was only effective at reducing PCB bioaccumulation in *C. pepo* after vigorously mixing the biochar into the soil, and Hartley et al. (2009) did not observe a substantial alteration in As uptake into *Miscanthus* foliage following biochar application.

As well as reducing contaminant bioaccumulation by lowering bioavailability, biochar has also been found to increase germination rates and reduce the phytotoxicity of contaminants to plants species. During early seedling establishment, Beesley et al. (2014) found that the germination and root length of *Lolium perenne* cultured in porewaters extracted from a former mine soil contaminated with As, Cd, Cu, Pb, and Zn was increased if the soil was first remediated by application of a biochar produced from the pyrolysis of orchard residues. Germination and root elongation of *Lepidium sativum* in contaminated sediment-soil mixtures polluted with both organic and inorganic contaminants was also improved by biochar

amendment (Jośko et al., 2013). Brennan et al. (2014b) showed an increase in maize (*Zea mays*) biomass and chlorophyll content after biochar produced form pine woodchip and maize stubble was added to soils contaminated with PAHs, As, Cu, and Zn. Furthermore, biochar promoted the development of fine maize roots, crucial to water and nutrient uptake in Cu- and As-contaminated soil (Brennan et al., 2014a). Houben et al. (2013a) found that the availability of Cd, Zn, and Pb to *Brassica napus* decreased with increasing biochar applications. Applications of 1% resulted in 100% mortality after 12 wk, but the 10% amended soils produced larger plants with lower metal concentrations than the 5% amended soils. The authors suggest that *B. napus* can be grown as an energy crop on contaminated land and the biomass pyrolyzed and returned to the soil to benefit remediation.

The introduction of plants to contaminated land helps to bind the soil and prevent erosion (Tordoff et al., 2000). Subsequently, by establishing a vegetative cover the risk of pollutants migrating off site to water courses is reduced (Robinson et al., 2009). There are several authors that report little or no increase in plant growth after biochar amendment alone, but an increase in plant growth when biochar is added alongside organic or inorganic fertilizers that cannot be explained by the fertilizer alone (Chan et al., 2007; Steiner et al., 2007; Van Zwieten et al., 2010; Yamato et al., 2006). Biochars, as well as immobilizing contaminants, can also affect the bioavailability of nutrients in soils. While some biochars can release nutrients into soils, it is often the case that nutrients in soil sorb to the biochar, which is why only modest increases in plant growth are observed after addition of biochar to unfertilized soils. When biochar is applied alongside fertilizer the biochar can reduce leaching and increase the efficiency of the fertilizers. In contaminated soils, biochar is able to reduce the toxicity of contaminated soil, improve plant germination rates, and reduce plant uptake of pollutants, but it can only increase plant biomass in soils where fertilizer is also applied (Fig. 4). Therefore, when applying biochar to remediate and revegetate contaminated soils it is recommended to apply in combination with fertilizer (Beesley et al., 2014; Beesley et al., 2011; Karami et al., 2011; Sizmur et al., 2011e).

Summary

Bioassays to assess the effect of biochar applications on the bioavailability of contaminants have chiefly employed earthworms and plants as test organisms. Some bioassays have revealed reductions in the uptake of metals by earthworms and plants, but several studies have failed to register significant reductions. These contrasting outcomes may be due to differences in the biochar sorpitive capacity, the bioavailability of contaminants in soil before application, species selection, and the biochar mixing regime. Biochar has been found to increase growth and reduce the symptoms of toxicity in plants but, contrastingly, reduce the growth of earthworms. Both plants and earthworms may benefit contaminated soil remediation because of erosion prevention and enhanced mixing of biochar and soil.

Field Experiments

Field experiments offer perhaps the best opportunity to test the performance of a biochar for the remediation of a contaminated soil in a measured and realistic way. By applying biochar to contaminated soils in situ, experiments are exposed to prevailing ambient conditions rather than the temporally homogenous

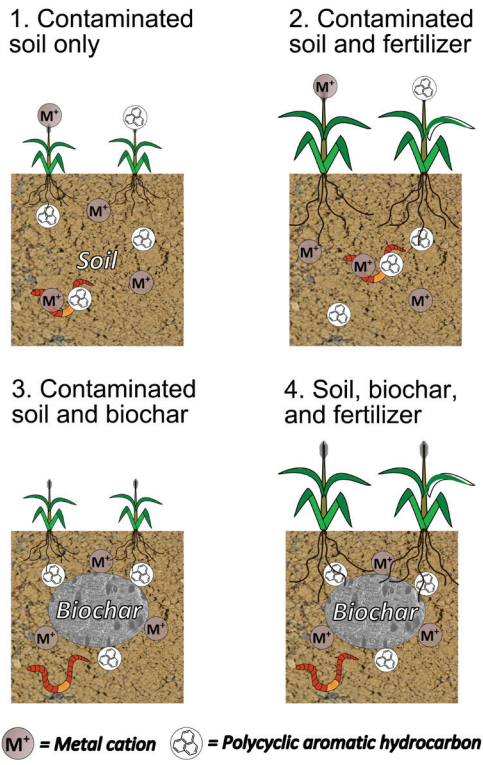

Fig. 4. Conceptual model of biochar and fertilizer applications to contaminated soils. When soil is unamended (1.) contaminants are taken up into plant and earthworm tissues. Fertilizer applications (2.) increase plant growth but not contaminant bioavailability. Biochar application (3.) reduces contaminant bioavailability, but only by adding biochar and fertilizer simultaneously (4.) is plant growth maximized while reducing the bioavailability of contaminants to plants and earthworms.

conditions provided by micro- and mesoscale laboratory and glasshouse trials. Biochar is incorporated into soils (or applied to the surface) in plots of a given area and then compared with biochar-free control plots (Bian et al., 2014). To account for the inherent variability of soils (particularly at contaminated sites, which are often more heterogeneous than arable soils), good statistical design must be employed (i.e., replication, randomization, and blocking) (Welham et al., 2014). To avoid cross-contamination, buffer strips are included between experimental plots (Hammond et al., 2013). Field experiments are usually costly to conduct, and the number of treatments that can be tested is often more limited than in laboratory experiments. Therefore, field experiments tend to only trial the use of biochars that have already undergone laboratory testing (i.e., batch sorption, soil incubations, or bioassays). Measurements can be made in each plot of a field experiment over time to test the performance of the remediation. For example, vegetation, invertebrates, porewater, or leachate can be surveyed or sampled, often simultaneously with climatic data collected from a local weather station.

Lessons Learned from the Field Application of Activated Carbon to Contaminated Sediments

For the reasons listed above, there are very few examples of field experiments in which biochar has been applied to contaminated soils, particularly those contaminated with organic pollutants. However, much can be learned from previous experiments that have assessed the potential for AC to remediate

contaminated sediments. For example, field pilots with AC have shown that it will take the carbon amendments several years to be fully effective in the field, as the mass transfer of HOCs from native organic matter onto introduced carbons can be a slow process, especially for the bulkier and more hydrophobic HOCs (Beckingham and Ghosh, 2011). Initial reductions in the field may therefore be more modest than predicted from initial well-mixed batch sorption studies; however, valuable information from AC pilot studies will enhance the effectiveness of biochars in future soil field pilots for HOCs. For example, the benefits of using the smallest particle size carbon practical (Zimmerman et al., 2005) and mixing the biochar into the soil effectively to speed up HOC mass transfer (Cho et al., 2009) will be equally applicable to biochar as they are for AC. Denyes et al. (2013) found no significant reductions in PCB bioaccumulation after manually mixing biochars and AC into soil, but did find significant reductions when the amendments were mechanically mixed into the soil for 24 h. Benthic organisms have been shown to help with this mixing in a process called bioturbation (Sun and Ghosh, 2007), so it likely that a rich soil fauna (e.g., earthworms) would also enhance biochar performance. The kinetics of mass transfer could be slower in soils than sediments, as mass transfer occurs through the aqueous phase and will therefore be minimal when the soil is dry. Therefore, keeping soils as water saturated as possible will also help contaminant transfer onto the biochar.

Biochar Applications to Contaminated Soils in the Field

Unlike organic contaminants, there are a few examples of field trials that use biochar to remediate metal contaminated soils. A suite of sequential cropping field experiments under a rice–wheat rotation that were designed to test the effect of biochar on the uptake of Cd from contaminated paddy fields in China have been recently reported (Bian et al., 2013). These were conducted in response to high levels of Cd found in rice from the region. Wheat straw biochar reduced the concentration of Cd in rice (Bian et al., 2014; Cui et al., 2011) and wheat (Cui et al., 2012) up to 3 yr after applications of 20 to 40 t/ha. The biochar increased the soil pH, reduced the $CaCl_2$ extractable Cd, and increased the soil organic carbon. The mass transfer of Cd from the soil to the biochar surfaces may have been faster in this experiment than experiments in arid environments because of the annual flooding inherent to rice paddies.

Beesley and Dickinson (2011) used a moderately polluted urban garden soil in the United Kingdom to study the impacts of a wood-derived biochar applied over the surface of the soil on the concentrations of metals, soluble C, and N in porewater at depths of 25, 50, and 75 cm below the soil surface. Their aim was to determine whether dissolved C from the weathering of biochar in situ, over the course of 1 yr, impacted on metal leaching and export from the soil profile by association of soluble C complexes. Soil was circumneutral in pH, 6% organic matter, and up to 30, 170, 360, and 450 mg/kg Cd, Cu, Zn, and Pb, respectively. Biochar caused similar increases in soluble carbon within the soil profile, as a comparative greenwaste compost amendment, but greatly increased As solubility. It was noted that the effects of the surface application of biochar, in common with greenwaste compost, only had an impact on the metal-organic carbon dynamics in the top 25 cm of soil profile, while lower depths were largely unaffected.

Summary

Field experiments enable researchers to demonstrate technology to practitioners and are not often used to unravel mechanisms or investigate hypotheses. Research on the application of biochar for soil remediation is in its infancy and there are only a few field experiments that specifically trial the application of biochar for this purpose. A suite of field experiments to remediate Cd-contaminated paddy fields in China have demonstrated that biochar can reduce Cd uptake by wheat. However, an experiment in the United Kingdom has demonstrated that biochar application to the surface of contaminated urban soils can increase the solubility of As deeper in the soil profile. Because research into the application of AC to contaminated sediments has progressed further than biochar applications to contaminated soils, lesson can be transferred and used to make recommendations. These recommendations include (i) reducing bicohar particle size as much as possible, (ii) thoroughly mixing biochar with soil mechanically or by encouraging earthworm activity, and (iii) keeping soil moisture as elevated as possible.

Implications for the Application of Biochar to Uncontaminated Agricultural Soils

Biochar inherently contains varying levels of organic pollutants such as PAHs, dioxins, or furans which are produced during pyrolysis (Garcia-Perez, 2008; Hale et al., 2012) and metals which are present in contaminated source material and concentrated after pyrolysis (Hossain et al., 2010; Kim et al., 2012; Matsuura et al., 2009). Therefore, the application of biochar to agricultural soil could potentially carry a significant risk to human health by contaminating soils used for growing crops or keeping livestock, unless appropriate measures are taken to minimize these risks.

Organic Contaminants Associated with Biochar

As discussed previously, biochar is particularly effective at adsorbing and sequestering organic contaminants (Beesley et al., 2010; Denyes et al., 2012; Gomez-Eyles et al., 2013b). As a result, enhanced sorption of hydrophobic organic compounds such as PAHs could decrease microbial mineralization by decreasing bioavailability to degrading organisms (Quilliam et al., 2013b; Rhodes et al., 2008, 2010; Song et al., 2012; Xia et al., 2010; Xin et al., 2014). This sorption is generally viewed as positive as it will result in reduced toxic effects by the contaminant and minimize HOC transfer up the food chain. However, when soil is contaminated with readily degradable or volatile organic compounds that could dissipate out of soils naturally (e.g., aliphatic hydrocarbons, low molecular weight PAHs, and chlorinated solvents), sorption to biochar may extend contaminant life time in the soil by reducing mineralization rates (Rhodes et al., 2008). On the other hand, some studies have found increasing degradation rates after biochar amendment (Qin et al., 2013; Sneath et al., 2013). This increased degradation is likely to be a consequence of biochar reducing the immediate toxicity of the freshly spiked contaminant to degrading bacteria. If contaminant bioavailability is not the limiting factor, the addition of biochar can help by reducing the risk of overloading the soil's biodegradation capacity (Bushnaf et al., 2011; Meynet et al., 2014). More recent research points toward coupling the reduced risk provided by contaminant sorption to

the biochar, with increased degradation by coating the carbon with contaminant degrading biofilms (Chen et al., 2012). The biochar surface could provide a source of high contaminant concentration for the organisms to feed on, and the biofilm would provide a suitable habitat for the bacterial community. Successful results have already been reported using this technology in ACs to enhance PCB dechlorination in impacted sediments (Kjellerup et al., 2014; Payne et al., 2013). However, a recent study of field-aged biochar in agricultural soil has demonstrated minimal natural colonization of the external (and internal) surfaces of wood-derived biochar (Quilliam et al., 2013a). Survival of a biofilm on biochar surface may therefore not be long enough to degrade contaminants because of the limitation of C in this particular niche (Quilliam et al., 2013a).

Despite having a strong sorption capacity for HOCs, biochar does not always decrease leaching, and in particular situations could actually increase the risk of HOC leaching if the application of biochar results in the release of considerable amounts of dissolved organic carbon (DOC) (Quilliam et al., 2013b). The sorption of HOCs to DOC and small pyrolyzed dust particles could also have other important downstream implications, (e.g., earthworm ingestion and subsequent bioaccumulation in food chains). Dissolved organic carbon release decreases with increasing biochar pyrolysis temperature and is also lower for hardwood source materials than grasses (Mukherjee and Zimmerman, 2013). This is consistent with recommendations given by Hale et al. (2012) that lower PAH and dioxin concentrations in biochars can be achieved by using woody source materials and pyrolyzing slowly (for several hours) at higher temperatures (between 500 and 600°C). Therefore, careful selection of source material and pyrolysis conditions will help to reduce the risk of HOC pollution when applying biochar to uncontaminated soils.

Inorganic Contaminants in Biochar

Certain source materials can contain significant levels of indigenous heavy metals (e.g., sewage sludge or preservative-treated waste wood), and as metals with high boiling points (e.g., Pb, Ni, Cu, Zn, and Cr) are rarely transferred into bio-oil or become volatilized (except Hg, As, Cd, and Se) during pyrolysis or combustion (Van Wesenbeeck et al., 2014), metal enrichment of biochar is inevitable (Hossain et al., 2010; Kim et al., 2012; Matsuura et al., 2009). Biochars produced from waste materials are inherently variable both spatially and temporally because of the variability in the composition of the source material. Yoshida and Antal Jr. (2009) found that biochar produced by pyrolyzing sewage sludge from a water treatment plant on the island of Oahu, Hawaii, contained metal concentrations below that preventing application to land. However, biochar produced from a nearby treatment plant on the same island contained elevated concentrations of Zn, Mo, and Cr that prevented their legal application to soils in Hawaii according to USEPA threshold values (Van Wesenbeeck et al., 2014). However, when cherry tomatoes were grown in soils amended with biochar produced from sewage sludge, the fruit was found to contain metal concentrations considerably lower than the Australian maximum permitted concentrations in food (Hossain et al., 2010). These findings indicate that although some biochars may contain elevated concentrations of metals, their bioavailability to plants is likely to be very low.

The consequences of applying biochar produced from contaminated waste wood source material are only now becoming evident (Lucchini et al., 2014a),

with implications for metal bioavailability and plant growth. Streams of waste wood, containing even small levels of preservative-treated wood used to produce biochar destined for soil application could pose a risk to soil quality and crop production, and pose a considerable environmental risk (Jones and Quilliam, 2014; Omil et al., 2007; Praharaj et al., 2002). Biochar made from waste wood source materials containing varying levels of contaminated timber can increase concentrations of soil available Cu, leading to changes in soil microbial community dynamics and uptake by crop plants. However, greater uptake does not necessarily result in a reduction of plant biomass. Subsequently, a thorough analysis of the source material intended for biochar production is critical before land application to avoid increasing the pollutant load of the soil or the availability or mobility of indigenous contaminants (Lucchini et al., 2014b; Madrid et al., 2007; Pérez-de-Mora et al., 2006). Recently, it has been demonstrated that biochar produced from waste forest residue contains an inherently low metal content (Lucchini et al., 2014b), and although biochar made from this source material caused small changes to metal fractionation, total metal concentrations in both soil and plant tissue remained unaltered.

Pesticides

In an agricultural context, the property of biochar that gives it such great potential for remediating contaminated sites (i.e., readily binding organic pollutants and heavy metals) can also significantly influence pesticide behavior in agricultural soils (Eibisch et al., 2015; Kookana, 2010). Sorption may decrease the efficacy of soil-applied agrochemicals by influencing their bioavailability and susceptibility to leaching, while the implications of biochar on pesticide behavior, particularly in the longer term, remains poorly understood (Cabrera et al., 2014). Biochar can induce the rapid and strong sorption of herbicides, which can reduce leaching, mineralization, and efficiency (Graber et al., 2012; Reid et al., 2013). Reduced leaching must be balanced with increased soil residence time since sorption to biochar may limit herbicide availability to microbial communities and suppress biodegradation in soils (Mello De Capitani et al., 2007). Evidence suggests that the effect of biochar on herbicide behavior is dependent on pyrolysis conditions, source material, and soil type (Sun et al., 2012b). Consequently, the longer term effects of biochar on pesticide sorption are unclear. Contrasting studies report either decreased sorption of herbicides by field-aged biochar (Martin et al., 2012) or the same effect as fresh biochar on sorption and microbial mineralization (Jones et al., 2011). Biochar application to soil, therefore, could potentially reduce the dissipation of foliar-applied pesticides and decrease the risk of human exposure and environmental contamination, but importantly could significantly affect the efficacy of soil-applied herbicides.

The Human Health Implications of Applying Biochar to Agricultural Soils

Although still poorly understood, there are several public health concerns associated with amending soil with biochar or wood ash. Breathing in small particles of biochar, either during its production or application, or after wind erosion from soil, can cause the serious respiratory disease pneumoconiosis (Mello De Capitani et al., 2007). The potential for biochar or wood ash dust to contain

considerable concentrations of metals further increases the risk to human health (Uski et al., 2012). Because of the difficulty in determining whether a source material is contaminated there is an urgent need for an improved understanding of the public health risk of applying biochar or wood ash to land, including irritation to eyes and mucous membranes by airborne pollutants (Vassilev et al., 2013). One potential strategy to lower human exposure is the pelletization of biochar and wood ash which would greatly reduce airborne particulate loss both pre- and postspreading, and may result in a better slow-release fertilizer (Gómez-Rey et al., 2012). However, this is likely to increase costs.

Contaminants applied to soils in biochar could also leach through soils and enter groundwater, or be ingested by soil organisms and biomagnify through food webs, causing toxicity at higher tropic levels. However, the greatest exposure risk comes from consuming crop plants that have accumulated considerable concentrations of metals in their edible parts. The potential for human exposure to toxic concentrations of metals will depend on the capacity for root uptake by individual crop species and the ability of the plant to sequester the contaminant without adversely effecting its growth. Uninformed growing (or grazing) of crops in soil amended with biochar made from a contaminated source material could potentially deliver toxic levels of metals to the human food chain.

Summary and Future

A large number of published studies have used batch sorption techniques to compare biochars, model sorption of contaminants on the surface of biochar, and to elucidate the mechanisms responsible. Laboratory incubations of biochar with contaminated soils have employed a wide range of chemical methods to assess the availability or mobility of contaminants after incubation. They have also revealed indirect effects of biochar on contaminant availability by, for example, modifying soil pH. Bioassays of earthworms or plants have been used in combination with chemical extractions to determine the impact of biochar on the bioavailability and bioaccessibility of contaminants in soil. The bioassays, in turn, must also consider the impact of the soil organisms themselves on the fate of contaminants sorbed to biochar surfaces. Only a small number of field trials have been conducted at contaminated sites to assess the use of biochar for soil remediation. Preliminary results are encouraging though, indicating that biochars are able to reduce metal contamination of edible crops grown on contaminated soils.

Because biochars are processed materials, they incur costs in time and energy to produce. Therefore, in the future biochars will be applied to land only if (i) they add value to agricultural systems (e.g., fertilizing crops), (ii) they reduce the prevalence of contaminants (e.g., remediating soils or safely disposing of contaminated feedstock), and (iii) they are as readily available and cost effective as other options (e.g., composts). A step back to consider the geographical and global context is required now that biochar research is maturing. There has been a technological and commercial push for biochar production without sufficient demand; in the future, biochars will only be produced where demand exists for them. Demand is likely to be for small batches of bespoke biochars designed for specific purposes, such as:

- Co-application with fertilizers, to prevent rapid leaching of nutrients to from soils to waters
- Remediation of soils and waters where contamination poses a risk to the environment
- Disposal of low value or contaminated feedstocks

Circularizing the production of biochar is likely to form the focus on the next decade of research. Biochars will increasingly be produced in situ where and when there is a demand for them. This will reduce the burden of transportation of feedstocks to and biochars from centralized production facilities, and develop local-scale or mobile, easily operable facilities producing biochars on demand and blending them with other waste products. There will still be a need for demonstration trials to prove the value of biochars and assess the environmental risks incurred by producing biochars from mixed sources. This will ensure that biochars are deployed to their maximum potential environmental value.

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